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Electrical Conductivity in Glass-Forming Solid Electrolytes: Theory and Experiment

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Abstract

A theory of the ionic conductivity in polymer electrolytes based on defect diffusion is evaluated using previously published data. Those data include the pressure and temperature variation of the electrical conductivity for poly(dimethylsiloxane-ethylene-oxide) complexed with NaCF_3COO . In the defect diffusion model, ion transport is controlled by defects and ion motion occurs when the ion is encountered by a single defect. As temperature is lowered or pressure increases, the number of single defects decreases thus decreasing the ionic conductivity. Further, there exists a pressure dependent critical temperature, T_c , below which single defects do not exist. It is shown how the pressure dependence of the conductivity is controlled by the pressure dependence of T_c . The theory is used to predict the variation with temperature of both the apparent activation volume and curvature in plots of the logarithm of the conductivity with pressure.

Keywords: Electrical Conductivity, Complex Impedance, High Pressure, Theory, Experiment

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1. Introduction

Several papers have appeared recently which discuss the effect of pressure on ionic conductivity in materials [1-6]. One quantity that is usually calculated from the pressure dependence of the conductivity is the apparent activation volume, ΔV_{app} , defined

$$\Delta V_{app} \equiv -kT \left[\frac{\partial \ln \sigma}{\partial P} \right]_T \quad (1)$$

where P is the pressure, k is Boltzmann's constant and T is the absolute temperature. As has been pointed out several times [3,7-9], in general, ΔV_{app} is different from the true activation volume, ΔV_{tru} , defined by

$$\Delta V_{tru} \equiv \left[\frac{\partial \Delta G^*}{\partial P} \right]_T \quad (2)$$

where ΔG^* is the Gibb's energy. The true and apparent activation volumes are the same only when the electrical conductivity exhibits Arrhenius behavior i.e. is given by

$$\sigma_{arr} = C \exp^{-\Delta G^*/kT} \quad (3)$$

where C is a constant. Clearly, this is not the case for most ion-conducting polymers since the electrical conductivity is usually non-Arrhenius. Nonetheless, with a few exceptions, ΔV_{app} and ΔV_{tru} are commonly used interchangeably because of the lack of an adequate theory connecting the two quantities. Part of the reason for this is that ΔV_{tru} has a straightforward physical interpretation as the volume change of the material required for ion transport. In fact, this suggests [3] the following relationship between ΔV_{tru} and the free volume, V_{fv} ,

$$\Delta V_{tru} + V_{fv} = \text{Constant} \quad (4)$$

On the other hand, the interpretation of ΔV_{app} depends upon the theory.

Recently, various theories which allow calculation and hence interpretation of ΔV_{app} have appeared. For example, Bamford et al. [6] have adapted the free volume theory of Cohen and Turnbull to describe ionic conductivity. The result of that work is that the conductivity is given by

$$\sigma_{fv} = A_1 \sqrt{T} \exp(-\gamma v^* / V_{fv}) \quad (5)$$

where A_1 , γ and v^* constants. From this equation, it follows that the apparent activation volume is given by

$$\Delta V_{app, fv} = -kT \chi_{fv} \ln \sigma_{fv} + A_2 \quad (6)$$

where A_2 is a constant and χ_{fv} is defined by

$$\chi_{fv} = -\frac{1}{V_{fv}} \frac{\partial V_{fv}}{\partial P} \quad (7)$$

Interestingly, $\Delta V_{app, fv}$ and ΔV_{tru} behave similarly vis a vis V_{fv} . Specifically, eqs. (4) and (6) show that both $\Delta V_{app, fv}$ and ΔV_{tru} increase as V_{fv} decreases and vice versa (The mathematical dependence is different in the two cases.). This explains the successful application of eq. (4) to activation volumes as given in ref. (3).

In addition, a theory based on defect diffusion [10-12] has recently been extended to include the effects of pressure on the ionic conductivity and applied to ionic conductivity, viscosity and dielectric relaxation in glass-forming materials near the glass transition temperature, T_g [13]. In the present note, further details of the application of defect diffusion theory to polymer electrolytes are given.

2. Defect Diffusion Theory

In the defect diffusion model, ion motion occurs when the ion is encountered by a mobile, single defect. As temperature is lowered the number of single defects decreases thus decreasing the ionic conductivity. Further, there exists a critical temperature, T_c , at which single defects cease to exist. (Only defect clusters exist below T_c .) Also, as pressure increases, defects are pushed closer together and become clustered so that the ionic conductivity decreases as pressure increases.

The details of the theory are given elsewhere [13]. For the purpose of the present note, the theory will be applied to the ionic conductivity using

$$\sigma_{DD}(T, P) = \frac{A_\sigma}{T(1-\delta)} \exp\left(-\frac{BT_c^{3/2}}{(T-T_c)^{3/2}(1-\delta)}\right) \quad (8)$$

where A_σ and B are assumed to be constant. $(1-\delta)$ describes the effect of pressure and temperature on the dimensions since the volume of the material, $V(T, P)$, is given by $V(T, P) = V_0(1-\delta)$ where V_0 is a constant. Next, for simplicity, it is assumed that δ is given by:

$$\delta = \chi(T)P - f(T)P^2 - g(T)P^3. \quad (9)$$

Finally, the critical temperature is assumed to be pressure dependent according to:

$$T_c(P) = T_c(0) + \left(\frac{\partial T_c}{\partial P}\right)P + \frac{1}{2}\left(\frac{\partial^2 T_c}{\partial P^2}\right)P^2 \quad (10)$$

This form is chosen as there appears to be a relationship between T_c and T_g and it is well known that there is usually a significant amount of curvature in the shift of T_g with pressure.

3. Reduction of Experimental Data

Previously reported data for poly(dimethylsiloxane-ethylene-oxide) (PDMS-EO) containing a sodium salt [14] are considered in the present work. The pressure derivatives of the electrical conductance, G , quoted in Ref. (15) were transformed to the pressure derivatives of the ionic conductivity as follows. The first derivative of the logarithm of the electrical conductivity is given by

$$\left(\frac{\partial \ln \sigma}{\partial P} \right)_{T,P=0} = \left(\frac{\partial \ln G}{\partial P} \right)_{T,P=0} + \frac{\chi}{3} \quad (11)$$

and the second derivative is given by

$$\left(\frac{\partial^2 \ln \sigma}{\partial P^2} \right)_{T,P=0} = \left(\frac{\partial^2 \ln G}{\partial P^2} \right)_{T,P=0} - \frac{2f}{3} + \frac{\chi^2}{3} \quad (12)$$

No PVT data (and hence values of χ and f) appear to exist for crosslinked PDMS-EO. As an alternative, the data for a related polymer, poly(ethylene glycol) mono methyl ether, were used [14]. Eq. (9) was best fit to the PVT data and values of χ and f were determined. Those values were then used in eqs. (11) and (12) to calculate the first and second derivatives of the logarithm of the electrical conductivity and the results are listed in Table 1. Eq. (1) was used to calculate the values of the apparent activation volume and those results are also listed in Table 1.

4. Zero Pressure Temperature Variation

Eq. (8) was best fit to the electrical conductivity data at zero pressure. The best fit parameters are $\log_{10}(A_\sigma)=0.0321$, $T_c = 140.9$ and $B=9.49$. The theoretical curve and experimental data are shown in Fig. 1. The agreement between theory and experiment is quite good.

5. Zero Pressure Apparent Activation Volume

Eqs. (8)-(10) were used to predict the apparent activation volume at zero pressure ($P=0$). The working equation is:

$$\Delta V_{app,DD} = kT \left[\frac{\chi B T_c^{1.5}}{(T - T_c)^{1.5}} - \frac{1.5 B T T_c^{0.5}}{(T - T_c)^{2.5}} \left(\frac{\partial T_c}{\partial P} \right) - \chi \right] \quad (13)$$

In this equation $T_c = T_c(0)$ except in the derivatives.

Eq. (13) was best fit to the data as described elsewhere [13]. The best value of $(\partial T_c / \partial P)$ is 57 K/GPa. This value along with the parameters determined from the fit to the data at zero pressure were used to predict the variation of the apparent activation volume with temperature and the result is shown in Fig. 2.

The agreement between the theory and experiment is quite good at low temperatures, near T_g . However, some difference is seen far above T_g . Discrepancy at higher temperatures is not surprising since the theory was derived to describe phenomena in the vicinity of T_g while the pressure data extend to temperatures as much as 140K above T_g . However, the results do not represent an accurate test of the theory since the compressibility is only approximate. In fact, the discrepancy occurs in the temperature range where the compressibility dependent terms are dominant. Consequently, the reason for the difference between the theory and experiment at high temperature remains to be determined.

The value of $(\partial T_c / \partial P)$ is within the range of the values of 87 and 48 K/GPa reported previously for PPG:NaCF₃SO₃ and PEG:NaCF₃SO₃ [1]. Next, it is reasonable that T_c is somehow related to T_g . Consequently, it would be of interest to compare

$(\partial T_c / \partial P)$ with $(\partial T_g / \partial P)$. Unfortunately, values of $(\partial T_g / \partial P)$ for ion-containing polymers have not been measured. However, an indirect comparison can be made with the pressure variation of T_g for one of the constituent pure polymers. A value of $(\partial T_g / \partial P) = 90 \text{ K/GPa}$ for high molecular weight (5×10^5) PEG has been reported [16]. Consequently, $(\partial T_g / \partial P)$ and $(\partial T_c / \partial P)$ are of the same order of magnitude.

In Ref. 3 (Fig. 11), it was pointed out that the apparent activation volume (at $P=0$) vs. logarithm of the electrical conductivity is approximately a straight line for PPG:LiCF₃SO₃. A similar plot for PDMS-EO containing NaCF₃COO is shown in Fig. 3 along with the predictions of the defect diffusion model via Eq. (8). It is seen that the agreement between the theoretical and the experimental results is good.

5. Zero Pressure Curvature

Next, the curvature in a plot of $\ln \sigma$ vs. pressure is considered. This quantity is of interest because it was recently pointed out that the values reported to that time were negative for PPG-based materials and positive for PEG-based materials [2]. More recent studies of PPG:NaCF₃SO₃ and PEG:NaCF₃SO₃ showed that the curvature is strongly temperature dependent, at least at low temperatures [1]. It was found that the curvature decreases with temperature so that at the lowest temperature studied, the curvature for PEG:NaCF₃SO₃ is negative [1]. It is clear from the results in Table 1 that the curvatures for PDMS-EO containing NaCF₃COO are negative.

As discussed elsewhere, negative curvatures are straightforward to explain in terms of free volume [1,3]. From Eq. (1), it follows that

$$\left(\frac{\partial^2 \ln \sigma}{\partial P^2} \right)_T = -\frac{1}{kT} \left(\frac{\partial \Delta V_{app}}{\partial P} \right)_T \quad (14)$$

Consequently, negative values are obtained if the apparent activation volume increases as pressure increases. This is expected since as pressure increases V_{fv} should decrease.

Positive values of the curvature will occur if V_{fv} increases with pressure. Specifically, it has been pointed out that the free volume is actually given by

$$V_{fv} = V_{mt} - V_{xclu} \quad (15)$$

where V_{mt} is the “empty” volume in the material and V_{xclu} is the “inaccessible empty” volume in the material [2,17]. Consequently, the free volume can increase with pressure if V_{xclu} decreases fast enough with pressure. A quantitative explanation in terms of free volume can be developed using Eq. (6).

Defect diffusion theory provides a simple explanation of the curvature in the ionic conductivity. Specifically, in the present application of the theory $(\partial^2 \ln \sigma / \partial P^2)$ is related to the curvature of T_c i.e. $(\partial^2 T_c / \partial P^2)$. In particular, Eq. (8) leads to:

$$\left(\frac{\partial^2 \ln \sigma_{DD}}{\partial P^2} \right)_{T,P=0} = +\chi^2 - 2f - \frac{1.5BTT_c^{0.5}}{(T-T_c)^{2.5}} \left(\frac{\partial^2 T_c}{\partial P^2} \right) + R \left(\frac{\partial T_c}{\partial P} \right) + Q \left(\frac{\partial T_c}{\partial P} \right)^2 + \frac{2fBT_c^{1.5}}{(T-T_c)^{1.5}} - \frac{2B\chi^2 T_c^{1.5}}{(T-T_c)^{1.5}} \quad (16)$$

$$\text{where } R = -\frac{1.5\chi BTT_c^{0.5}}{(T-T_c)^{2.5}} - \frac{1.5\chi BT_c^{0.5}}{(T-T_c)^{1.5}} - \frac{1.5\chi BT_c^{1.5}}{(T-T_c)^{2.5}} \quad (17)$$

$$\text{and } Q = -\frac{0.75BTT_c^{-0.5}}{(T-T_c)^{2.5}} - \frac{3.75BTT_c^{0.5}}{(T-T_c)^{3.5}} \quad (18)$$

Again, $T_c = T_c(0)$ except in the derivatives.

Despite the complexity of the formalism, the interpretation is straightforward since only the third term in Eq. (16) is adjustable. (All other terms are either determined by the

bulk properties of the material or by the zero pressure temperature variation of $\ln(\sigma)$ and its first derivative with pressure.) In fact, Eq. (16) easily yields negative values of $(\partial^2 \ln \sigma / \partial P^2)$ since only the first and sixth terms in Eq. (15) are positive. For the present materials, the first term is very small and the sixth term is not sufficient to overcome the negative terms. To demonstrate this, we let $(\partial^2 T_c / \partial P^2) = 0$ so that the third term is zero. The resultant defect diffusion value of $(\partial^2 \ln \sigma / \partial P^2)$ is -28 K/GPa^2 at 262.2 . This value is more negative than the experimental value at 295K of -10.4 GPa^{-2} . Consequently, less negative (and positive) values of $(\partial^2 \ln \sigma / \partial P^2)$ occur if a negative value of $(\partial^2 T_c / \partial P^2)$ is used in Eq. (16). (Justification for a negative value of $(\partial^2 T_c / \partial P^2)$ will be given later in this section.) In fact, the data are reproduced reasonably if $(\partial^2 T_c / \partial P^2) = -65 \text{ K/GPa}^2$. This value was used in Eq. (8) to predict values for $(\partial^2 \ln \sigma / \partial P^2)$ vs. temperature (at $P=0$) and the results are plotted in Fig. 4. There is good agreement between experiment and the predictions of defect diffusion theory.

The value of $(\partial^2 T_c / \partial P^2) = -65 \text{ K/GPa}^2$ is between the values of -135 and -47 K/GPa^2 reported previously for $\text{PPG}:\text{NaCF}_3\text{SO}_3$ and $\text{PEG}:\text{NaCF}_3\text{SO}_3$ [1]. It would be of interest to compare $(\partial^2 T_c / \partial P^2)$ with $(\partial^2 T_g / \partial P^2)$. However, no data for $(\partial^2 T_g / \partial P^2)$ are available for comparison with $(\partial^2 T_c / \partial P^2)$ for ion-containing polymers. However, the results can be compared with $(\partial^2 T_g / \partial P^2)$ for a related constituent polymer containing no salt. Specifically, a value of -146 K/GPa has been reported for high molecular weight PEG [15]. Consequently, the value of $(\partial^2 T_c / \partial P^2)$ is reasonable in both sign and magnitude.

6. Summary

In summary, defect diffusion theory is applied to ionic conductivity data for PDMS:EO containing NaCF_3COO . Those data include the pressure and temperature variation of the ionic conductivity. It is shown how the pressure dependence of the conductivity is controlled by the pressure dependence of the critical temperature T_c . The theory is used to predict the apparent activation volume and its variation with temperature. In addition, the curvature in plots of the logarithm of the conductivity vs. pressure is calculated. Good agreement between theory and experiment is obtained.

Acknowledgments

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Table 1.

This table contains experimental values of the pressure derivatives of the electrical conductivity and apparent activation volumes at $P=0$ for PDMS-EO containing

NaCF_3COO . The values of $\left(\frac{\partial \ln \sigma}{\partial P}\right)_T$ and ΔV are slightly different from those reported in Ref. 14 because of the corrections due to PVT data.

$T(\text{K})$	$\left(\frac{\partial \ln \sigma}{\partial P}\right)_T (\text{GPa}^{-1})$	$\left(\frac{\partial^2 \ln \sigma}{\partial P^2}\right)_T (\text{GPa}^{-2})$	$\Delta V (\text{cm}^3/\text{mol})$
262.2	-20.1	-10.4	43.8
266.5	-18.7	-6.8	41.5
272.3	-17.2	-7.0	38.9
280.5	-14.9	-3.5	34.8
306.6	-10.1	-2.6	25.7
317.9	-8.86	-1.5	23.4
323.4	-8.48	-0.33	22.8

Figure Captions

Fig. 1. Electrical conductivity/resistivity vs. reciprocal temperature for PDMS-EO containing NaCF_3COO . The squares represent the experimental data and the solid line is the prediction of defect diffusion theory.

Fig. 2. Apparent activation volume vs. absolute temperature for PDMS-EO containing NaCF_3COO . The squares represent the experimental data and the solid line is the prediction of defect diffusion theory.

Fig. 3. Apparent activation volume vs. the logarithm of the electrical conductivity PDMS-EO containing NaCF_3COO . The squares represent the experimental data and the solid line is the prediction of defect diffusion theory.

Fig. 4. Second derivative of the logarithm of the electrical conductivity with respect to pressure at $P=0$ vs. absolute temperature for PDMS-EO containing NaCF_3COO . The squares represent the experimental data and the solid line is the prediction of defect diffusion theory.

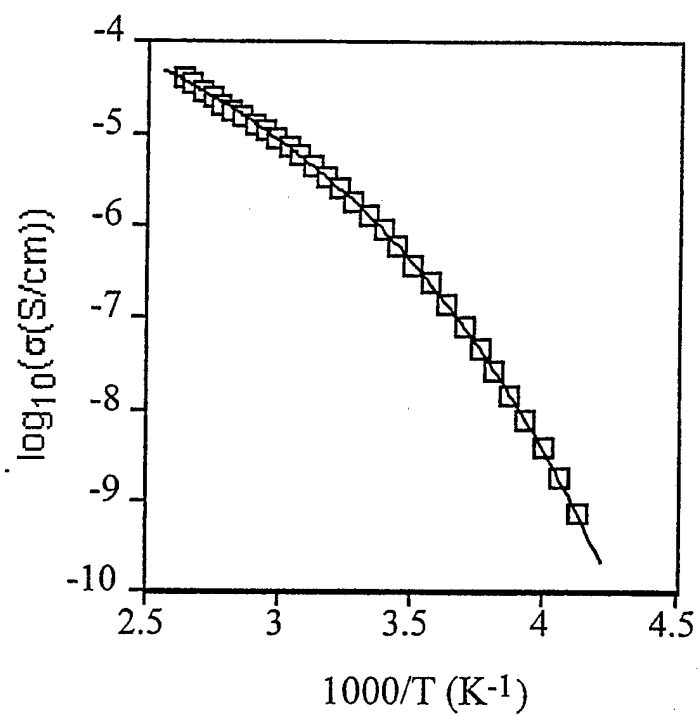


Figure 1

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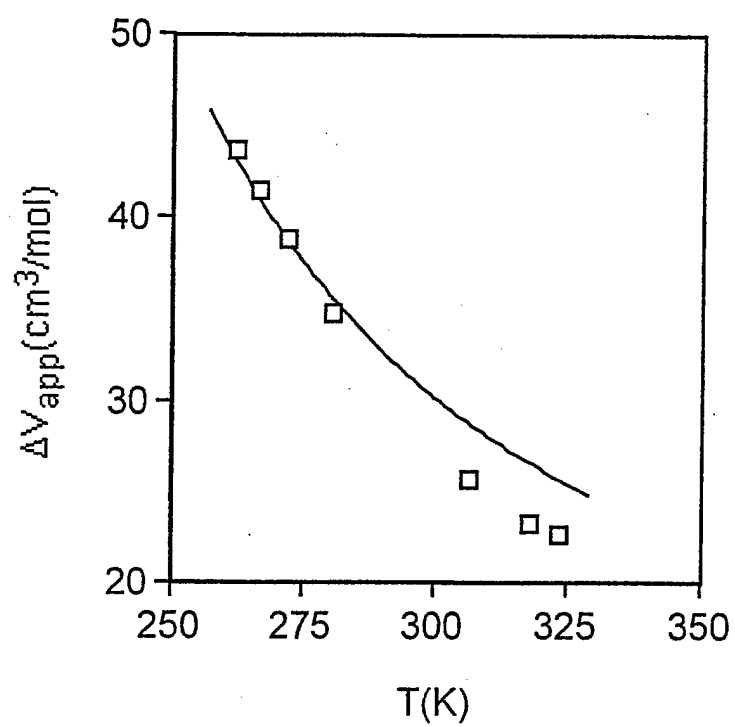


Figure 2

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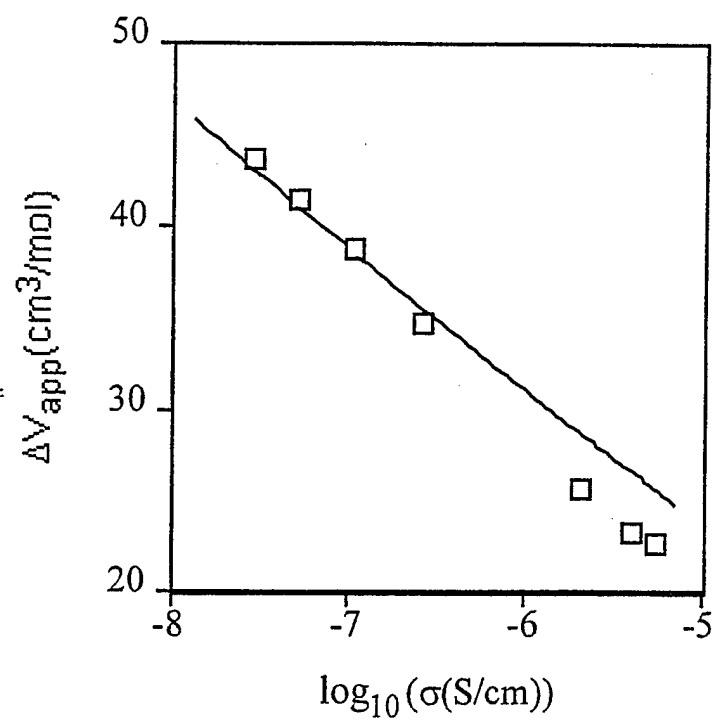


Figure 3

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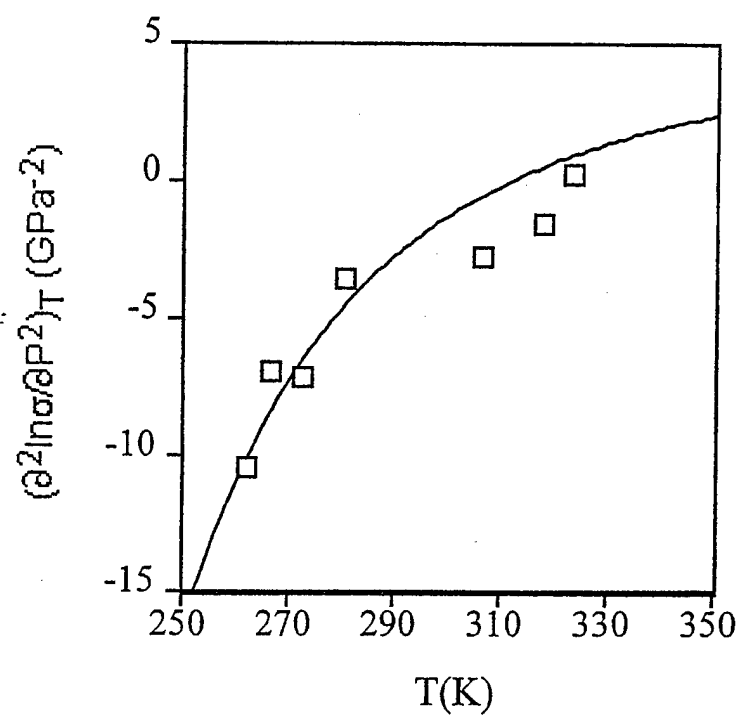


Figure 4

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